Implementation of a Monte Carlo method to model photon conversion for solar cells

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Abstract

A physical model describing different photon conversion mechanisms is presented in the context of photovoltaic applications. To solve the resulting system of equations, a Monte Carlo ray-tracing model is implemented, which takes into account the coupling of the photon transport phenomena to the non-linear rate equations describing luminescence. It also separates the generation of rays from the two very different sources of photons involved (the sun and the luminescence centers).

The Monte Carlo simulator presented in this paper is proposed as a tool to help in the evaluation of candidate materials for up- and down-conversion. Some application examples are presented, exploring the range of values that the most relevant parameters describing the converter should have in order to give significant gain in photocurrent.

1. Introduction

The ability of photon converters to modify the light spectrum has found widespread use in the fields of fluorescent lighting, lasers, displays, etc. In particular, by down-conversion, high-energy photons are absorbed and re-emitted in a larger number with lower energy while by up-conversion, the excitation with low energy photons leads to the emission of higher energy photons

Photon converters are also being considered as a means of improving the spectral response of solar cells by conditioning the solar spectrum A down-converter deposited on top of a solar cell will redistribute incident photons with energies greater than twice the solar cell bandgap into more than one lower energy photon, so that they are more efficiently used. On the other hand, an up-converter turns sub-bandgap photons, which were already transmitted through the solar cell, into higher energy photons, which, upon reflection, may be used by bifacial solar cells.

As calculated by Trupke and co-workers by detailed balance calculations, a maximum conversion efficiency of 39.6% may be achieved for a 6000 K blackbody spectrum and a down-converter with one intermediate level and 47.6% achieved with an improved up-converter . The calculations have been extended to the case of illumination from the AM1.5G spectrum, both with the bandgap of the cell as an optimisation parameter and at a fixed value of 1.1 eV, which corresponds to that of silicon Efficiencies of 37.7% (for a down-converter), and 38.6% (for an up-converter) are calculated for this last case.

The detailed balance model is a very powerful tool for calculating the thermodynamic limits of cell performance, but because of the idealisations involved in the analysis, more insight into the potential of practical converters can be given through alternative approaches, such as the one undertaken in this paper.

Moreover, as low gains have been observed until now when incorporating an up-converter under a bifacial solar cell it may be relevant to analyze carefully the precise mechanisms involved in the photon conversion, and characterize candidate materials to discard or recommend them for photovoltaic applications.

A quantitative model is proposed in this paper to help in the characterization of converter materials. It takes into account both the transport of photons and their absorption and emission by the active centers in the converter. Among the possibilities to calculate the optical properties of the converters numerically a Monte Carlo approach has been chosen. Monte Carlo simulations have been carried out for up-conversion in erbium-doped materials in previous works but our implementation is different in order to address the special characteristics of photovoltaic applications.

2. Photon conversion phenomena

A converter layer consists of a non-absorbing host material in which luminescent centers are dissolved, or present as powders glued to the material. When propagating inside the layer, light will follow straight lines in the first case, while in the second it will experience multiple reflections at internal interfaces, which may be treated in a simple way as elastic scattering events.

In this context, the variation rate of light propagating in the converter depends on three terms: the light that is lost as a result of absorption by the luminescent centers, the light that is emitted as a result of radiative transitions between the energy levels of the centers, and the light scattered at a certain point from all directions. A formal treatment of the phenomena is described elsewhere

Absorption and emission resulting from luminescence can be described by considering the simple luminescent center as a series of energy levels, see for example the three energy level in Fig. 1, which also represents several processes leading to up-conversion. Solid lines represent photon-induced transitions and dashed lines indicate energy transfer between centers. The solid grey line corresponds to photon emission. The graph can help in understanding how the most usual conversion processes take place; in particular, ground state absorption (GSA) (a), excited state absorption (ESA) (b) or energy transfer (ET) (c and d). for details. A similar graph can be drawn up for down-conversion, based on the reverse processes.

The dynamics of luminescence can then be described through the so-called rate equations (RE). In the system in Fig. 1 they take the form:

$$\frac{dN_0}{dt} = -N_0\Phi_a + N_1\frac{1}{\gamma_a\tau_a} - N_0\Phi_e + N_2\frac{1}{\gamma_e\tau_e} + k_{\mathrm{cf}}N_1^2$$
$$-k_{\mathrm{cr}}N_0N_2 + k_{\mathrm{df}}N_1^2N_0 - k_{\mathrm{dr}}N_0^2N_2$$
$$\frac{dN1}{dt} = N_0\Phi_a - N_1\frac{1}{\gamma_a\tau_a} - N_1\Phi_b + N_2\frac{1}{\gamma_b\tau_b} - 2k_{\mathrm{cf}}N_1^2$$
$$+2k_{\mathrm{cr}}N_0N_2 - 2k_{\mathrm{df}}N_1^2N_0 + 2k_{\mathrm{dr}}N_0^2N_2N_t = N_0 + N_1 + N_2 \tag{1}$$

In writing the above equations, neither stimulated emission nor multiphonon absorption has been taken into account. In them:

- N_k (cm^{-3}) is the concentration of luminescent centers in state k, N_t being the total number of them
- τ_i (s) is the radiative lifetime for transition labeled i
- $0 \le \gamma_i \le 1$ is the efficiency of radiative transitions i when non-radiative transitions are present
- Φ_i (s^{-1}) is the rate of photon-induced transition i
- k_{cf}, k_{cr} ($\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$) are kinetic coefficients for transitions c
- k_{df}, k_{dr} ($\mathrm{cm}^6 \cdot \mathrm{s}^{-1}$) are kinetic coefficients for transitions d.

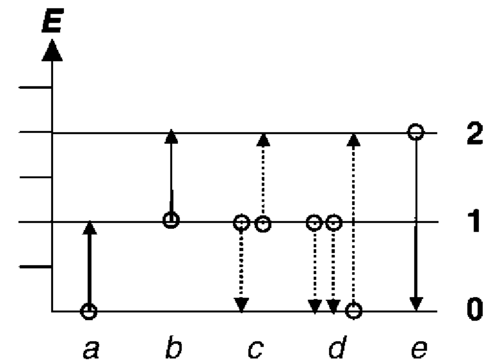

Fig. 1. Simplified details of several processes leading to up-conversion. The energy levels are labeled 0, 1 and 2. The solid lines represent photon-induced transitions; dashed lines indicate energy transfer between centers. The solid grey line corresponds to photon emission. The open circle shows the initial state of the center.

A detailed balance establishes that well-defined relationships must hold between the coefficients of a process and their time-reversal. Note, however, that the RE (Eq. (1)) are not written for single energy levels but for groups of them, connected by faster thermalization processes that are not accounted for. Hence the above coefficients are phenomenological quantities with no straightforward connection to fundamental magnitudes.

3. The Monte Carlo approach

Ray tracing is a common method for integrating the photon transport equation at optical frequencies, presenting the ability to deal with complex geometries and scattering events as a main advantage. In photon converters, however, this equation is coupled to the non-linear, first-order rate equations describing luminescence, so that an iterative procedure has to be developed.

Another issue that should be taken into account in our problem is that there are two sources of photons of different kinds: one is the sun, and the other the luminescence centers, and the number of photons generated by the first one is much higher than the one generated by the second. If rays were traced using the same distribution for both kinds, the ones corresponding to the luminescent source would be scarcely represented. That is why a multicanonic Monte Carlo technique [17] has been implemented, by separating the generation of rays from the two sources, and making a subsequent adjustment.

The principles of the implemented simulation algorithm, whose flow is detailed in Fig. 2, are presented below.

The domain is first divided into small regions $v = 1,2,...V$. For plane-parallel geometry, these are thin slices within which the state of the centers will be assumed to be uniform.

At the beginning of the process luminescent centers are assumed to be in the ground state, $N_0^{\,v} = N_t$. Before photons can be traced, the absorption coefficient in the region v for every possible transition k must be calculated as

$$\alpha_k^v = N_{k,\mathrm{low}}\sigma_k \tag{2}$$

with σ_k (cm^2) the photon capture cross section for transition k.

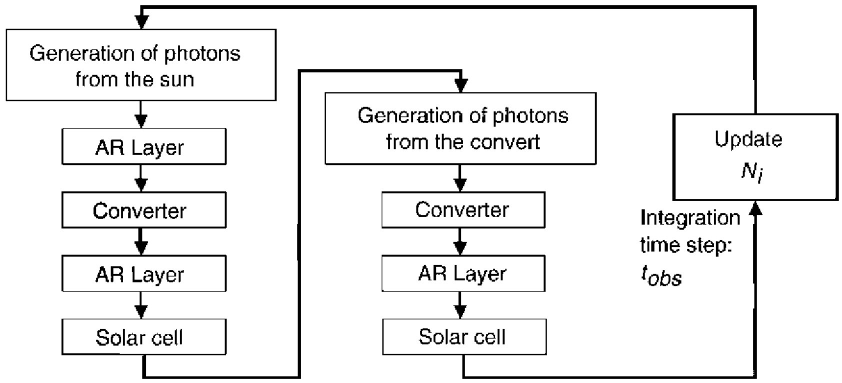

Fig. 2. Flow of the simulation procedure for down-conversion. In the case of up-conversion, the "Converter" and "Solar cell" positions in the first column are exchanged.

P_1 photons are then traced from the illumination spectrum, given its spectral and angular distributions. If we are dealing with an up-converter located at the rear of the solar cell, photons are first traced through the cell. Reflection and transmission in the interfaces between the anti-reflection coatings and the substrate, as well as absorption in those layers, is taken into account.

Once they are transmitted through the interface, they enter the converter material, within which the following events may take place:

1. Scattering. This is a random change of direction, characterized by a scattering length α_d; after this, the photon is not lost, but continues to be traced.
2. Absorption by transition k in slice v. The photon disappears and the event information is stored.
3. Reflection at the converter interfaces. The photon can be lost or transmitted to the cell, disappear, or reflected back to be traced again.

After that, P_2 events from the excited levels are generated. Each possible transition is assigned a probability proportional to its rate, according to the terms included in Eq. (1). Some of these events lead to the isotropic emission of a photon whose frequency is randomly chosen according to the shape of the emission line. This photon is then treated as previously explained for external photons.

Let ϑ_1 be the total rate of arrival of external photons (s^{-1}) and r_n^v the rate (s^{-1}) at which a given event n takes place in region v of the converter. In our procedure, we assume a certain "observation time" t_{OBS} (the time step for the integration of the rate equations). Within this time interval, the state of the luminescent centers, and hence the absorption coefficients, are kept constant, so that the outcome of the tracing of the P_1 external photons is scaled by $\vartheta_1 t_{OBS}/P_1$ and the results of the P_2 phosphor-related events by

$$f = \frac{t_{OBS}}{P_2}\sum_{n,v} r_n^v. \tag{3}$$

These numbers are used to update the state of the centers: if N centers have emitted a photon according to a transition, the population of the initial level is decreased by $N\times f$ and that of the final level is correspondingly increased, and so on.

Populations of the different states are compared before and after the tracing sequence. If the deviation is consistently small, tracing is finished and the obtained emission and up-conversion rates for the last batch are the final result. Otherwise, we start again by tracing external and internally-generated photons, as previously described.

Note that the value of t_{OBS} is somewhat arbitrary; if it is too small, a large number of iterations will be needed to reach the steady-state; if it is too big, the convergence may not be assured. It has at least, to be shorter than the characteristic time of the evolution of the centers.

4. Discussion of the model results

To study the potential gain in photocurrent in a solar cell when converter layers are implemented on it, a sensitivity analysis of the influence of the different set of parameters describing the converter properties has been carried out. The starting point is data within the range of that found in literature for rare-earth doped materials, together with assumptions of our own (see Table 1).

Some results are presented in the following paragraphs, first for an up-converter and then for a down-converter. The maximum increase in photocurrent as a result of the converted

Table 1
Parameters describing the converter layers. The starting point is based on the values of Er-doped layers found in the literature

	Up-converter	Down-converter
E_{01}; E_{12} (eV)	0.8; 0.5	1.35; 1.15
$N_{Converter}$	2	2
N_t (cm^{-3})	10^{20}	10^{20}
σ_{01}; σ_{02}; σ_{12} (cm^2)	6×10^{-21}; 0; 6×10^{-21}	0; 6×10^{-21}; 0
k_{cf}; k_{cr} (cm^3 s^{-1})	4×10^{-18}; 0	0; 0
τ_{10}; τ_{20}; τ_{21} (s)	∞; 3×10^{-5}; ∞	3×10^{-5}; ∞; 3×10^{-5}
η_{10}; η_{20}; η_{21}	1; 1; 1	1; 1; 1
$\Delta\lambda$ (nm)	50	50

Numerical sub-indices refer to energy levels between which transitions occur. N_{Conv} is the index of refraction of the converter and $\Delta\lambda$ the range of convertible wavelengths around a central λ_0.

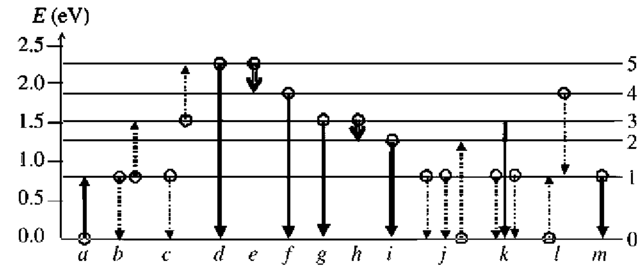

Fig. 3. Erbium energy levels (referenced to the ground state $^4I_{15/2}$, labeled as 0) and different excitation and relaxation processes (a to l) after The full, black, arrow pointing upwards is photon absorption; the grey arrow pointing downwards denotes photon emission; dotted arrows indicate energy transfers between neighboring ions; double-line arrows (e and h) denote multiphonon, non-radiative transitions. The reverse processes are not represented.

photons is given, assuming the cell quantum efficiency is one at the conversion wavelengths.

4.1. Up-converter layers

A three-level system of the kind presented in Fig. 1 is considered. Although it may seem simple, it can represent with enough accuracy for our purpose experimental up-converters. Fig. 3, for example, details the relevant levels and important transitions of an erbium-doped oxide, whose use is being proposed for silicon solar cells Among them, we will consider only pumping *a* from ground state with low energy photons (≅ 1530 nm), the energy transfer *b* that drives the ion to state 3, that then relaxes very rapidly through multiphonon emission *h* to level 2 from where it decays *i* with the emission of a higher energy (≅ 980 nm) photon.

Table 2
Potential increase in photocurrent for an up-converter with an optimistic set of parameters

	Up-converter
N_t (cm^{-3})	10^{22}
σ_{01}; σ_{02}; σ_{12} (cm^2)	6×10^{-17}; 0; 6×10^{-17}
k_f; k_r (cm^3 s^{-1})	4×10^{-15}; 0
τ_{10}; τ_{20}; τ_{21} (s)	∞; 3×10^{-5}; ∞
η_{10}; η_{20}; η_{21}	1; 1; 1
$\Delta\lambda$ (nm)	150
Concentration level	1000
ΔJsc (A/cm^2)	6.5×10^{-3}

Fig. 4 summarises the sensitivity analysis carried out by sweeping in some of the parameters while maintaining others. It shows how up-conversion benefits from higher luminescent center concentrations, a wider range of absorbed wavelengths and higher capture cross section. It also shows the non-linearity of up-conversion as a function of the incident photon flux, which is related to the squared dependence of the ET process on the population in level 1.

The potential gain in photocurrent is small, as can be seen, especially for low concentration levels. So, it is relevant to test other materials, with more appropriate parameters. As an example, Table 2 shows that a hypothetical up-converter material characterized by an "optimistic" set of parameters can give only a gain of 6.5 mA/cm^2 if operating at 1000 suns. Unrealistic solar

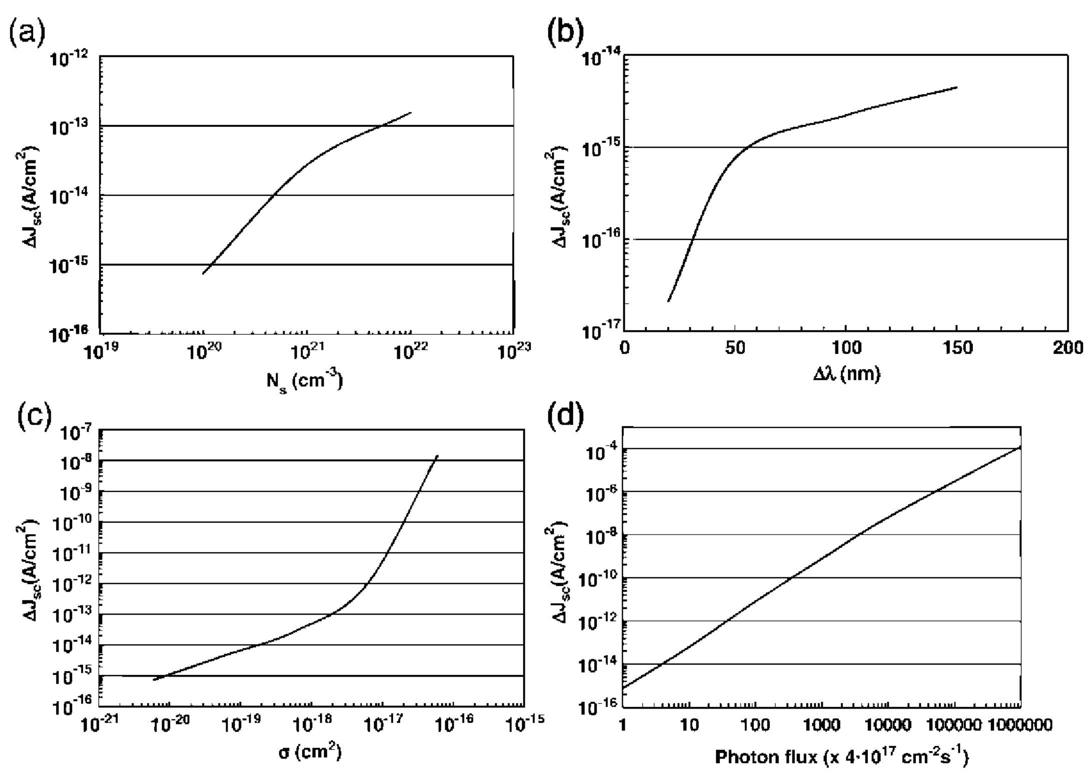

Fig. 4. Potential gain in short-circuit current for a solar cell with an up-converter at the rear. The cell quantum efficiency is assumed to be one at the conversion wavelengths. Dependence on luminescent center concentration (a), range of convertible wavelengths (b), photon capture cross section (c) and concentration level (d).

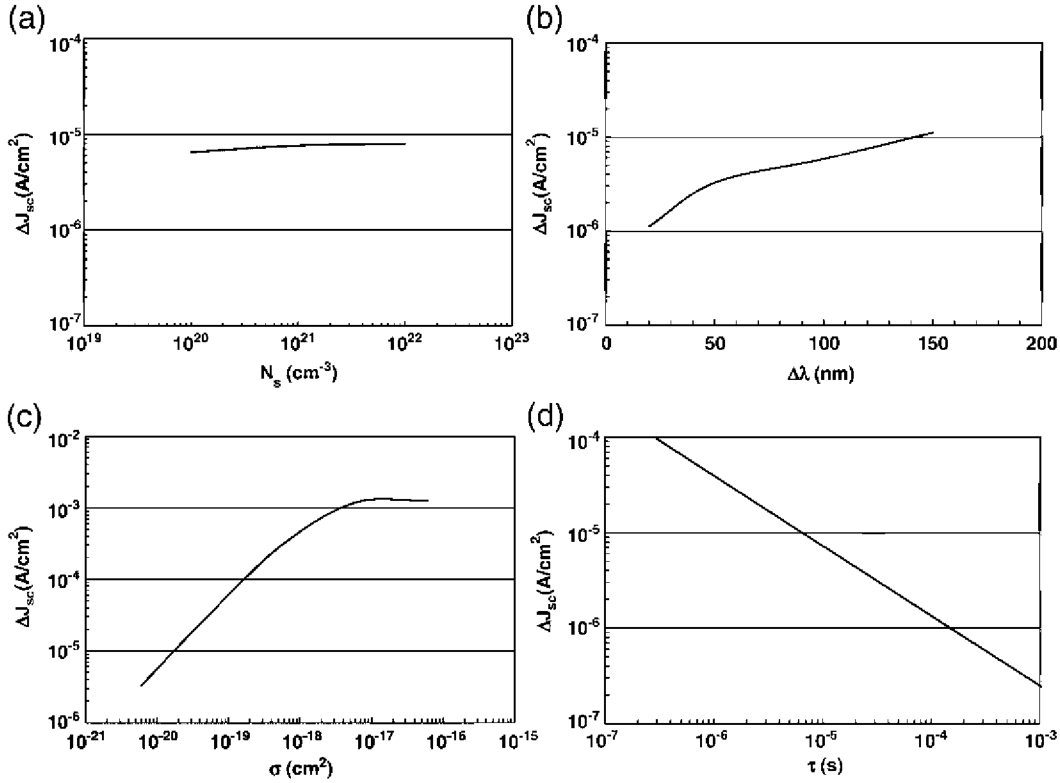

Fig. 5. Potential gain in short-circuit current for a solar cell with a down-converter on it. The cell quantum efficiency is assumed to be one at the conversion wavelengths. Dependence on luminescent center concentration (a), range of convertible wavelengths (b), photon capture cross section (c) and emission lifetimes (d).

concentrations should be reached to achieve significant increase in photocurrent, as already pointed out

4.2. Down-converter layers

A similar analysis is carried out for a down-converter layer. Note that in this case the exercise is somewhat arbitrary, because most of the down-converting systems that have been studied to date seem unlikely to be suitable for application to terrestrial silicon solar cells because the excitation energies required are too high . But in our opinion it is also meaningful because it can give guidelines to evaluate candidate materials that may be proposed.

Some results are shown in Fig. 5. When giving the potential gain in photocurrent, the fact that the high-energy photons would contribute to the current if they were not converted, is taken into account.

The luminescent center concentration is not so relevant for down-conversion, but it increases with the range of converted wavelengths, as well as with photon capture cross section, until a value is reached where the emission and ET processes are limiting. Obviously, the quicker the radiative transitions emitting photons, the better.

Although modest, the potential gain in photocurrent is higher than for the up-converter, with a similar range in the parameter values. Besides, the influence of concentration is not relevant, which is expected taking into account the linear dependence of down-conversion with photon flux.

A hypothetical down-converter characterized by more convenient parameters (see Table 3) would increase the short-circuit current by 7 mA/cm^2, a significant gain for devices at present.

5. Conclusions

A model is built to describe photon conversion phenomena, by taking into account the dynamics of luminescence and light propagation in the converter. The proposed model is useful to assess the conversion efficiency of different materials, indicating the characteristics a converter should have to give significant gain in quantum efficiency.

There is still lot of work to be done to take advantage of converter layers for solar cells. Their intrinsic properties have to

Table 3
Potential increase in photocurrent for a down-converter with an optimistic set of parameters

	Down-converter
N_t (cm^{-3})	10^{22}
σ_{01}; σ_{02}; σ_{12} (cm^2)	0; 6×10^{-17}; 0
k_f; k_r (cm^3 s^{-1})	0; 0
τ_{10}; τ_{20}; τ_{21} (s)	3×10^{-7}; ∞; 3×10^{-7}
η_{10}; η_{20}; η_{21}	1; 1; 1
$\Delta\lambda$ (nm)	150
Concentration level	1
ΔJsc (A/cm^2)	7×10^{-3}

be clearly evaluated to see if they absorb and emit a significant number of photons. Furthermore, in the case of up-conversion based on rare-earth doped materials, the process needs high photon fluxes to enhance the absorption phenomenon.

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